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Synthesis and Charactrization of $PrMno_3$ Cathode Material for Intermediate Temperature Solid Oxide Fuel Cells

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Abstract

Praseodymium manganite cathode material $PrMnO_3$ was obtained by assisted combustion method at a temperature of 600 °C using aspartic acid as fuel. This process remarkably reduced the synthesis time and temperature. The obtained nano crystalline structure of $PrMnO_3$ powder was confirmed by XRD studies. The nano particle size was confirmed by X-ray line broadening analysis using the Scherrer equation. Thermal decomposition behavior of the as prepared powder was carried out by thermo gravimetry analysis. The thermo gravimetric profile of the as prepared powder showed a weight loss for the sample prepared with aspartic acid with the higher combustion temperature. The surface morphology of $PrMnO_3$ was investigated by SEM analysis. The synthesized material showed reasonable electrical conductivity and the four probe dc technique was used to determine the electrical conductivity of $PrMnO_3$ nano powder.

Key words*: *Assisted combustion method; Cathode material; IT-SOFC; $PrMnO_3$.

1. INTRODUCTION

The solid oxide fuel cell (SOFC) has attracted much attention due to their high energy conversion efficiency, low pollution and ability to use hydrocarbon fuels. Cathode material in SOFC has been intensively studied because they make great contribution to the output losses in the cell. The high operating temperature of about 1000°C with the zirconia-based electrolyte leads to a limited choice of interconnect materials, thermal expansion mismatch and chemical reactivity among the components (Minh, 1993; Tsai and Barnett, 1997). These difficulties could be minimized by reducing the operating temperature to an intermediate range 500-800°C (Lee and Manthiram, 2005). The cathode material of the SOFC at reduced operating temperature has to meet several requirements like high electrical conductivity, thermal expansion behavior and chemical compatibility with the electrolyte and high catalytic activity for oxygen reduction. In addition, the cathode with a porous structure has to allow oxygen to diffuse to the reaction sites. For better electronic conductivity and thermal expansion coefficient to the YSZ electrolyte perovskite type $PrMnO_3$ is the most investigated cathode material.

Several synthesis methods have been developed for the preparation of perovskite powers such as solid-state reaction, some solution methods for example, sol-gel process, co-precipitation technique and citrate process (Bell *et al.* 2000; Zhang *et al.* 2000; Chick *et al.* 1990; Conceicao *et al.* 2009). The combustion method is particularly useful in the production of ultrafine ceramic powders with small average particle size and high porosity. This is a simple method with the advantage of using inexpensive precursors and resulting nano sized, homogeneous and highly reactive powders (Patil *et al.* 2002; Varma *et al.* 1998).

In this work, we have attempted the synthesis of $PrMnO_3$ nano crystalline powder by combustion

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process. This paper discusses the improvement in cathode performance on electrical conductivity, XRD – analysis and SEM analysis towards YSZ electrolyte. The thermo gravimetric profile of the as prepared powder showed a weight loss for the sample prepared with aspartic acid with the moderate combustion temperature. The nano crystalline powder has excellent characters for various applications such as ceramics, gas sensor, rechargeable ceramic batteries, SOFC etc. In addition they can significantly enhance the sintering rates, decreases the sintering temperature and improve the optical, electrical and magnetic properties compared to the micro meter size powders.

2. EXPERIMENTAL STUDIES

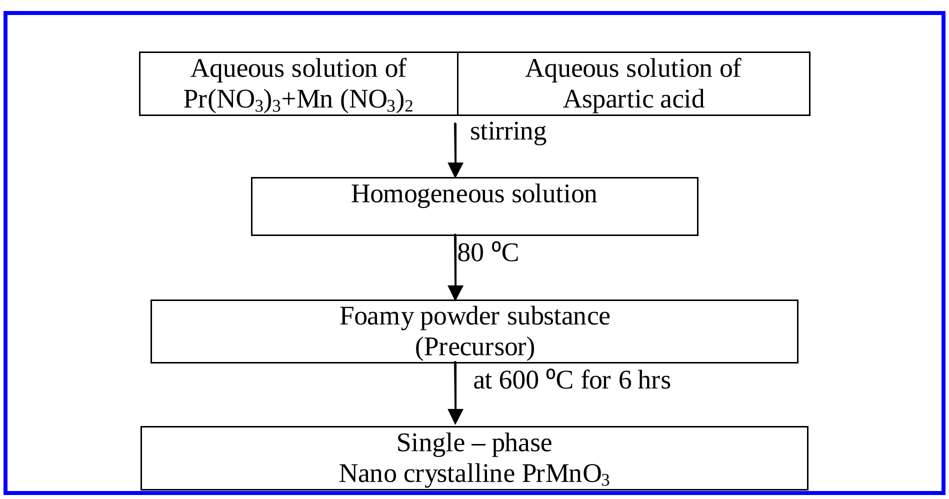
$PrMnO_3$ Cathode material was synthesized by assisted combustion process. This process involves the dissolution of desired amount of Pr $(NO_3)_3$, Mn $(NO_3)_2$ and aspartic acid (fuel) with high purity in small quantity of water in order to form homogeneous solution. The solution was stirred well and then heated at 80 °C. After the solution reached the point of spontaneous combustion, it is started to burning and become a solid. The combustion process was not complete until all the flammable substances are consumed and the resulting material is a foamy powder substance. This powder exhibiting voids and pores formed by escaping gases during combustion reaction. The foamy powder substance was crushed in a pestle and mortar. The crushed powder was kept in a mufftle furnace (EDG 3000 3P) at 600 °C for 6 hrs.

The ignition time and combustion temperature were measured during the synthesis with a thermocouple (K type) (Conceicao *et al.* 2011) inserted in the reagent mixture. The stoichiometric amount of the propellant was determined by calculation based on the valencies of oxidizing and reducing elements as determined by the propellant chemistry (Ringueda *et al.* 2001).

3. CHARACTERIZATION

The structural study and the determination of the lattice parameters of the oxides were performed by X- ray diffractometer using CuKα radiation. The XRD data were collected by step scanning in the range $20 \leq 2\theta \leq 80$ in the increment of 0.02^{o} 2θ. The lattice parameters were determined using a least squares unit cell refinement computer program (Kostogloudis and Ftikos, 1999). X – Ray (CuKα) diffraction analysis was carried out on the powder samples in order to identify the phase composition, purity and structural confirmation. The particle size was calculated from XRD line broadening by using Scherrer equation. The electrical conductivity was measured in air by standard four probe DC method in the temperature range of 200-700 ^{o}C.

Thermo gravimetric analysis (TGA) data of as prepared powders were carried out using a TA thermal analyzer (SDT Q600 model), with a heating rate of 2 ^{o}C min^{-1} from room temperature to 1000 ^{o}C in air (Conceicao *et al.* 2011). Micro structural characterization of the cathodes and interfacial reaction analysis were carried out with JEOL LSM-5610 scanning electron microscopy (SEM) equipped with an Oxford Instruments INCA Energy 200 X-ray detector for elemental analysis by energy dispersive spectroscopy (Lee and Manthiram, 2005).



Depending on the TGA measurement, above 1000 °C the mixed original material has finished the weight loss and thermal effect. Therefore the mixture was calcined at 600 °C for 6 hrs and cooled then well grained into a fine powder for the preparation of disc (pellets). The surface morphology of the sample was observed by using SEM analysis. The electrical conductivity of sintered pellets ($PrMnO_3$) was measured by standard DC four probe techniques.

4. RESULT & DISCUSSION

4.1 X- ray diffraction studies

In order to investigate the chemical compatibility of $PrMnO_3$ cathode material, the X-ray diffraction study was made on the powders which were calcined at 600 °C for 6 hrs in a mufftle furnace. Significant peaks which represent the $PrMnO_3$ have been appeared. The peaks become sharper which indicate the formation of phase pure $PrMnO_3$.

It has been known that $PrMnO_3$ retains the orthorhombic perovskite structure. The X - ray diffraction pattern of $PrMnO_3$ sample which was calcined at 600 °C for 6 hrs in a mufftle furnace is shown in fig.1. The sample calcined for 6 hrs exhibits a single phase without any noticeable impurity phase. Consequently the X - ray diffraction results strongly suggest that assisted combustion reaction method requires much lower calcinations energy with shorter time duration than solid state reaction method where the calcinations temperature is usually 800 °C to 1000 °C for more than 6 hrs.

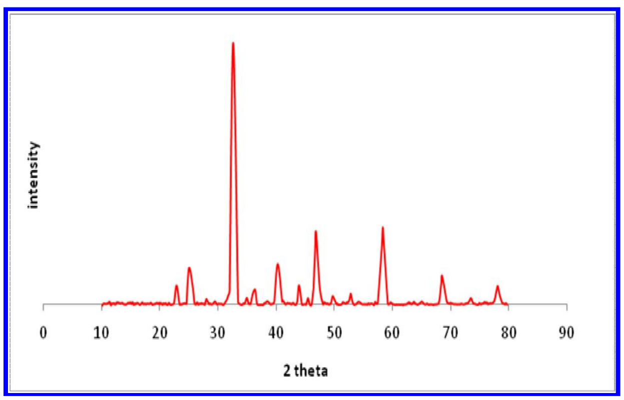


Fig. 1: XRD pattern of assisted combustion synthesis of $PrMnO_3$

From the x - ray diffraction data of the prepared $PrMnO_3$ powder, the average particle size was calculated from x – ray line broadening analysis using Scherrer equation,

$$D = \frac{0.9\,\lambda}{\beta \cos\theta}$$

Where D is the crystallite size in nm, λ is the radiation wave length (for CuKα radiation, λ =1.54 A°), β is the broadening of the line (half width) in radians and θ is the diffracting peak angle. The average crystallite size values of $PrMnO_3$ nano powder synthesized by assisted combustion reaction was 24 nm (12.68 nm). The particle size measured from XRD data. The smaller average crystallite size (nano particle) was achieved by using assisted combustion method compared to conventional solid state reaction method.

4.2 Thermal analysis

Fig. 2 shows TGA curves of the as synthesized $PrMnO_3$ powder before calcinations. Thermal decomposition takes place in three stages and burn out of organics is complete at about 750 °C. The first decomposition stage at 300 °C, can be assigned to the loss of adsorbed water, the second stage at about 450 °C - 600 °C, can be associated with the decomposition of combustion residues mainly fuel that was not burnt during the fast combustion reaction and the third at 750 °C may be due to complete dissociation of carbonates produced during combustion and initiation of the formation of $PrMnO_3$ phase.

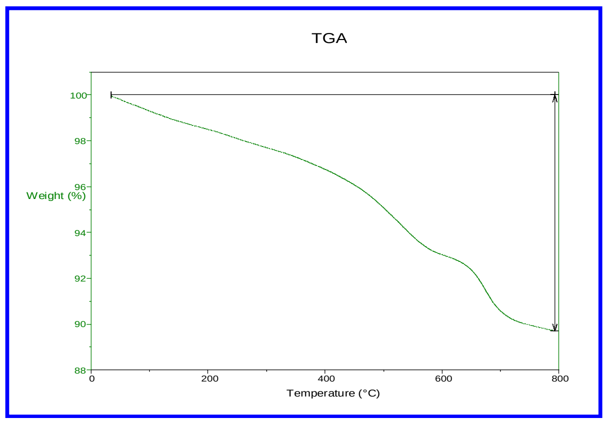


Fig. 2: TGA curves of PrMnO3 powder prepared by the combustion method

4.3 SEM analysis

The microstructure of $PrMnO_3$ powder was synthesized by assisted combustion reaction method and calcined at 550 °C for 5 hrs as shown in fig. 3. It can be seen that the porosity of $PrMnO_3$ was found to be 30.08 % calcined at 500 °C beyond this temperature (550 °C) the porosity was decreased to 18.19%. A fine particle size and the porosity of ≈ 30% are required for the cathode to promote the mass transfer of the oxidant gas effectively. The $PrMnO_3$ calcined at 550 °C can produce a porous cathode for IT-SOFC applications.

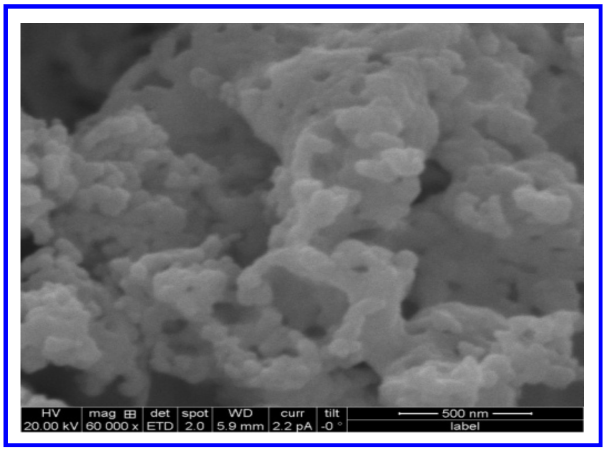


Fig. 3: SEM image of as prepared $PrMnO_3$

4.4 Electrical conductivity

Generally there are two kinds of conductive mechanism namely electronic and ionic conductivity in $PrMnO_3$ type perovskite oxides due to the presence of porous and oxygen vacancies. Since the ionic conductivity is much lower than the electrical conductivity, it can be assumed reasonable that the measured values refer to the electronic conductivity.

The logarithm of electrical conductivity (log σ) of the system as a function of the reciprocal temperature is shown in fig 4. It indicates that the maximum electrical conductivity of the sintered sample is 450 Scm^{-1} at 550 ^oC for $PrMnO_3$ nano crystalline powder.

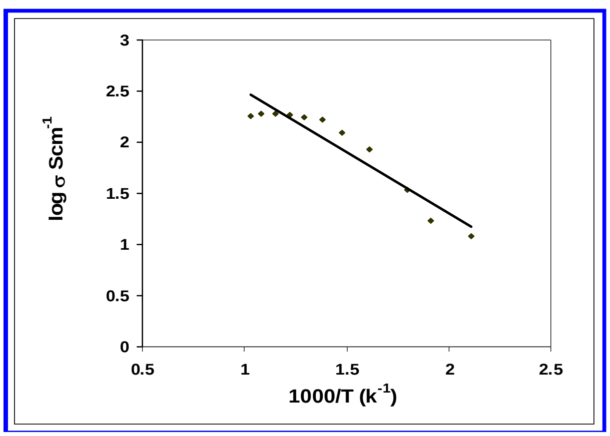


Fig. 4: Electrical conductivity of $PrMnO_3$

5. CONCLUSION

A combustion synthesis process has been used to prepare $PrMnO_3$ nano crystalline powder. According to our results thermal behavior, phase formation and crystallite size are strongly dependent on the nature of the fuel (aspartic acid) and heating temperature. The combustion reaction is more complete with aspartic acid, attaining moderate temperature and generating less organic residues. $PrMnO_3$ phase formation, with secondary phases, was observed when aspartic acid was used as fuel because the reaction is less violent, promoting increased formation of gases which greatly contributes to obtain materials of high crystallinity with nanometric dimensions. The synthesized nano powders have nano particles with high specific area. In addition electrical conductivity measurement revealed that the maximum conductivity of 450 Scm^{-1} was obtained in air at 550 ^oC which is higher than the reported values.

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